

CLAIMS

What is claimed is:

1. A method for producing single wall carbon nanotube products comprising the steps of:
 - 5 (a) providing a high pressure CO gas stream;
 - (b) providing a gaseous catalyst precursor stream comprising a gaseous catalyst precursor that is capable of supplying atoms of a transition metal selected from Group VI, Group VIII or mixture thereof, said gaseous catalyst precursor stream being provided at a temperature below the decomposition temperature of said catalyst precursor;
 - 10 (c) heating said high pressure CO gas stream to a temperature that is (i) above the decomposition temperature of said catalyst precursor and (ii) above the minimum Boudouard reaction initiation temperature, to form a heated CO gas stream; and
 - (d) mixing said heated CO gas stream with said gaseous catalyst precursor stream in a mixing zone to rapidly heat said catalyst precursor to a temperature that is
 - 15 (i) above the decomposition temperature of said catalyst precursor, (ii) sufficient to promote the rapid formation of catalyst metal atom clusters and (iii) sufficient to promote the initiation and growth of single wall nanotube by the Boudouard reaction, to form a suspension of single wall carbon nanotube products in the resulting gaseous stream.
- 20 2. The method of claim 1, further comprising the step of passing said suspension of single wall nanotube products through a growth and annealing zone.
3. The method of claim 1 or 2 further comprising the step of separately recovering said single wall carbon nanotube products from said resulting gaseous stream.
4. The method of claim 1 further comprising the step of supplying a
 - 25 nucleation agency to said mixing zone to facilitate the rapid formation of said catalyst metal atom clusters.
5. The method of claim 4 wherein said nucleation agency is a gaseous metal-containing compound.

6. The method of claim 5 wherein said gaseous metal-containing compound is selected from the group consisting of $\text{Ni}(\text{CO})_4$, $\text{W}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, or mixtures thereof.

7. The method of claim 4 wherein said nucleation agency is laser light photons.

5 8. The method of claim 1 wherein said catalyst precursors is a metal-containing compound of a metal selected from the groups consisting of tungsten, molybdenum, chromium, iron, nickel, cobalt, rhodium, ruthenium, palladium, osmium, iridium, platinum and mixtures thereof.

9. The method of claim 8 wherein said metal-containing compound is a
10 metal carbonyl.

10. The method of claim 9 wherein said metal carbonyl is selected from the group consisting of $\text{Fe}(\text{CO})_5$, or $\text{Co}(\text{CO})_6$ and mixture thereof.

11. The method of claim 1 wherein said high pressure CO gas stream is provided at a pressure of about 3 atm to about 1000 atm.

15 12. The method of claim 11 wherein said high pressure CO gas stream is provided at a pressure of about 10 atm to about 100 atm.

13. The method of claim 1 wherein said gaseous catalyst precursor stream is supplied in a high pressure CO gas stream.

14. The method of claim 13 wherein the partial pressure of said catalyst
20 precursor in said high pressure CO gas stream is from about 0.25 Torr to about 100 Torr.

15. The method of claim 14 wherein said partial pressure of said catalyst precursor is from about 1 Torr to about 10 Torr.

16. The method of claim 1 wherein said gaseous catalyst precursor stream is supplied at a temperature in the range of from about 70°C to about 200°C.

25 17. The method of claim 1 wherein said high pressure CO gas stream is heated to a temperature in the range of from about 850°C to about 1500°C.

18. The method of claim 17 wherein said temperature is from about 900°C to about 1100°C.

19. The method of claim 1 wherein said mixing step is effective to heat said catalyst precursor stream to the desired temperature in less than about 10 milli-sec.

20. The method of claim 19 wherein said mixing step is effective to heat said catalyst precursor stream to the desired temperature in from about 1 to 1000 μ sec.

5 21. The method of claim 1 wherein said catalyst precursor is heated to a temperature in the range of from about 850°C to about 1250°C in said mixing zone.

22. The method of claim 2 wherein said growth and annealing zone is maintained at a temperature in the range of from about 850°C to about 1250°C.

10 23. The method of claim 3 wherein said single wall carbon nanotube products are recovered by passing said suspension through a gas-permeable filter.

24. The method of claim 3 wherein said single wall carbon nanotube products are substantially free of solid contaminates other than catalyst atoms.

25. The method of claim 24 wherein said single wall carbon nanotube products are at least 99% single wall carbon nanotubes.

15 26. The method of claim 3 wherein the recovered single wall carbon nanotube products have a tube diameter in the range of from about 0.6 nm to about 0.8 nm.

27. The method of claim 26 wherein said single wall carbon nanotube products comprise (5,5) tubes.

20 28. The method of claim 1 further comprising the step of controlling the diameter of the single wall carbon nanotube products recovered by controlling the catalyst cluster size at the time the growth reaction is initiated.

29. The method of claim 28 wherein said catalyst cluster size is controlled by a method selected from the group consisting of:

- 25 (a) controlling the presence of CO(P_{CO}) in the mixing zone;
- (b) controlling the temperature in the mixing zone;
- (c) controlling the partial pressure of the gaseous catalyst precursor (P_{CAT}) provided to the mixing zone;
- (d) controlling the partial pressure of gaseous nucleating agents (P_N) provided to the mixing zone; or

(e) mixtures of the foregoing.

30. A single wall carbon nanotube product made by the process of any of claims 24, 25, 26 or 27.

31. The single wall carbon nanotube products of claim 30 which comprises
5 ropes.

32. An apparatus for producing single wall carbon nanotube products comprising:

(a) a high pressure reaction vessel comprising in serial communication a reactant introduction in zone, a reactant mixing zone, a growth and annealing zone and a
10 product recovery zone;

(b) a first reactant supply conduit for supplying a heated high pressure CO gas to said introduction zone;

(c) a second reactant supply conduit for supplying a gaseous catalyst precursor to said information zone;

15 (d) mixing means for rapidly and intimately mixing the gas flows from said first and second reactant supply conduits as said flows enter said mixing zone;

(e) heating means for maintaining said growth and annealing zone at an elevated temperature; and

(f) gas/solids separation means positioned in said product recovery zone to
20 remove solid single wall carbon nanotube products from the gas flows exiting said growth and annealing zone.

33. The apparatus of claim 32 further comprising a high pressure CO gas preheater for heating the gas in said first reactant supply conduit.

34. The apparatus of claim 33 wherein said CO gas preheater comprises a heat
25 source thermally coupled to portion of said first reactant supply conduit.

35. The apparatus of claim 34 wherein said heat source is the growth and annealing zone.

36. The apparatus of claim 34 wherein said heat source is a resistive heating element positioned in said reactant introduction zone.

37. The apparatus of claim 32 further comprising cooling means for cooling the gas in said second reactant supply conduit.

38. The apparatus of claim 32 further comprising a cooling means for cooling the product recovery zone.

5 39. The apparatus of claim 32 further comprising a laser and means for directing the output of said laser to impinge on said mixing zone.

40. The apparatus of claim 32 further comprising a heated enclosure surrounding at least the growth and annealing zone portion of said reaction vessel.

41. The apparatus of claim 32 wherein said gas/solids separation means
10 comprises a gas-permeable filter element.

42. The apparatus of claim 32 wherein said mixing zone is maintained at a first predetermined pressure and said growth and annealing zone and said product recovery zone are maintained at a second predetermined pressure.

43. The apparatus of claim 39 wherein said laser is directed downstream along
15 the axis of said reaction vessel into said mixing zone.

44. The apparatus of claim 39 wherein said laser is directed upstream along the axis of said reaction vessel into said mixing zone.

45. The apparatus of claim 39 wherein said laser is directed transversely to the axis of said reaction vessel into said mixing zone.

20 46. A composition of matter comprising single-wall carbon nanotubes having a tube diameter in the range of 0.6 nm to 0.8 nm.

47. The composition of claim 46 wherein at least 95% of the SWNTs in said composition have a diameter in the range of 0.6 nm to 0.8 nm.

48. The composition of claim 46 wherein at least 75% of the SWNTs in said
25 composition have a diameter in the range of 0.6 nm to 0.8 nm.

49. The composition of matter of any of claims 46, 47 or 48 wherein said nanotubes are present as ropes.

50. The composition of matter of any of claims 46, 47 or 48 wherein said nanotubes are present (5,5) single-wall carbon nanotubes.

51. A composition of matter comprising (5,5) single-wall carbon nanotubes.
52. The composition of claim 51 wherein at least 50% of said SWNTs are (5,5) tubes.
53. The composition of claim 51 wherein at least 25% of said SWNTs are
5 (5,5) tubes.
54. The composition of matter of any of claims 51, 52 or 53 wherein said nanotubes are present as ropes.